UDC 548.737

TIN(IV) PORPHYRIN COMPLEXES. CRYSTAL STRUCTURES OF meso-TETRAPHENYLPORPHYRINATOTIN(IV) DIACETATE, BIS(DICHLOROACETATE), BIS(TRIFLUOROACETATE) AND DIFORMATE, AND STRUCTURAL CORRELATIONS FOR TIN(IV) PORPHYRIN COMPLEXES WITH O-BOUND ANIONIC LIGANDS

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Structures of four tetraphenylporphyrinatotin(IV) bis(carboxylato) complexes [Sn(tpp)(OCOR)$_2$] have been determined by single crystal X-ray diffraction. All complexes have typical octahedral geometry. The average Sn—N bond lengths for R = CH$_3$, CHCl$_2$, CF$_3$ and H are 2.091, 2.084, 2.082 and 2.086 Å, respectively. The Sn—O bond lengths are 2.096, 2.091, 2.109 and 2.090 Å respectively. These bond lengths and those of all other reported Sn(tpp) complexes of O-bound anionic ligands are compared. There is an inverse correlation between the Sn—N and Sn—O bond lengths, indicating that stronger electron donation by the axial anionic ligand results in an expansion of the porphyrin core. Correlation of the Sn—O bond lengths with the pK$_a$ of the conjugate acids of the axial ligands shows that the stronger the acid, the longer the Sn—O bonds, indicating that the bonding is dominated by electrostatic effects.

K e y w o r d s: tin porphyrins, X-ray crystallography, carboxylato complexes, structure correlations.

INTRODUCTION

The tin(IV) centre in octahedral tin(IV) porphyrin complexes is strongly oxophilic and stable complexes are readily formed with carboxylate or aryloxide ligands [1]. These neutral complexes are easily handled in organic solvents. In recent years [Sn(por)X$_2$] complexes have been employed in a variety of contexts, particularly as building blocks for generating supramolecular constructs [2—17], taking advantage of the ease of formation of the axial tin-oxygen bonds. Some years ago, our group studied various structural correlations for complexes [Sn(tpp)X$_2$] (H$_2$tpp = 5,10,15,20-tetraphenylporphyrin; X = O-bound anionic ligand), using data from NMR (^{1}H [18—20] and ^{119}Sn [21]), UV/visible [18] and Raman spectroscopies [22], and from X-ray crystal structure determinations [23, 24]. One correlation we explored was between the in-plane Sn—N bond distances and the axial Sn—O (anionic ligand) bond distances, which are inversely related [1]. There was one significant outlier point, namely the Sn—N bond distances in [Sn(tpp)(OAc)$_2$] (**1**). The structure of this species was reported by Chen and co-workers for a bis(acetic acid) solvate [25]. The reported Sn—N distances are 2.197(5) and 2.068(4) Å, of which the former lies well outside the range expected for carboxylato complexes of tin(IV) porphyrins. Even the average is very long compared with close analogues. On the other hand, the Sn—O distance of 2.086(5) Å does lie in the vicinity of the data for other carboxylato complexes.

We have reinvestigated the complex (**1**) and solved its structure using a crystal free of acetic acid, and find that in this case the Sn—N distances lie well within the range expected. To extend the corre-
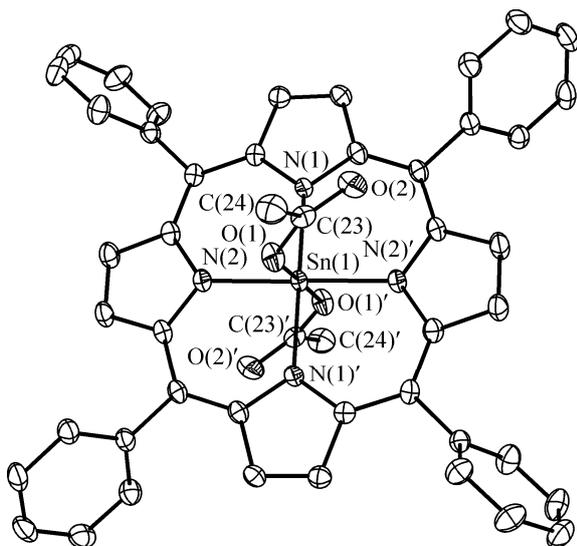
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Fig. 1. ORTEP depiction of (**1**)·2CH$_2$Cl$_2$. The molecule has crystallographic inversion symmetry. The hydrogen atoms and dichloromethane molecules have been omitted for clarity. Thermal ellipsoids are plotted at the 40 % probability level. Symmetry operation: ^{i} $-x+2$, $-y+1$, $-z+1$

lations further, we have also determined the structures of the analogous bis(dichloroacetato) complex [Sn(tpp)(OCOCHCl$_2$)$_2$] (**2**), the bis(trifluoroacetato) complex [Sn(tpp)(OCOCF$_3$)$_2$] (**3**) and the diformato complex [Sn(tpp)(OCOH)] (**4**). These results are reported herein, together with further consideration of the correlations we reported previously, since more crystallographic data have become available in the four years since our review [1].

EXPERIMENTAL

The samples were available from our previous work [19—21]. Crystals of (**1**)·2CH$_2$Cl$_2$ were grown by diffusion of pentane into a dichloromethane solution, and crystals of (**2**)·2CHCl$_3$, (**3**)·2CHCl$_3$ and (**4**)·1.5CHCl$_3$ were obtained by layering hexane over chloroform solutions.

X-ray crystallography. Reflection data for (**1**)·2CH$_2$Cl$_2$, (**2**)·2CHCl$_3$, (**3**)·2CHCl$_3$ and (**4**)·1.5CHCl$_3$ were collected under the software control of CrysAlis CCD [26] at 173(2) K on an Oxford Diffraction Gemini Ultra diffractometer using MoK_α radiation generated from a sealed tube. Data reduction was performed using CrysAlis RED [26]. The structures were solved by direct methods using SIR97 [27] then refined with SHELXL-97 [28]. Multi-scan empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm, within CrysAlis RED [26]. Ordered non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were included in idealised positions and refined using a riding model. Data collections on several crystals of (**4**)·1.5CHCl$_3$ were carried out and all showed signs of non-merohedral twinning. The best data set was used for the structure refinement presented herein. A reasonable (though not ideal) multi-scan absorption correction was applied but as a result of the twinning T_{min}/T_{max} values (0.675/0.904) lie outside the calculated range (0.813/0.904) for the crystal. Crystal data and refinement details are reported in Table 1 and ORTEP-3 [29] depictions are provided in Figures 1—3. The CIF files have been deposited with the Cambridge Structural Database (CCDC reference numbers 711425-711428) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

[Sn(tpp)(OAc)$_2$] crystallised in the monoclinic space group $P2_1/n$ along with two dichloromethane molecules ((**1**)·2CH$_2$Cl$_2$). The complex, illustrated by ORTEP depiction in Fig. 1, has $\overline{1}$ crystallographic symmetry. The tin(IV) centre, as with all complexes reported herein, is octahedral with axially coordinated anionic counterions (in this case acetate). The macrocyclic ring of the ligand is almost perfectly planar and the metal resides in the mean plane of the N$_4$ coordination sphere as it must by crystallographic symmetry.

The bis(dichloroacetato) complex [Sn(tpp)(OCOCHCl$_2$)$_2$] (**2**) and the bis(trifluoroacetato) complex [Sn(tpp)(OCOCF$_3$)$_2$] (**3**) crystallise with two chloroform molecules per complex in isostructural arrangements and in crystals that are almost isomorphous (space group $P\overline{1}$, see Table 1 for cell de-

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Crystal and refinement data for the structures of (**1**)·2CH$_2$Cl$_2$, (**2**)·2CHCl$_3$, (**3**)·2CHCl$_3$ *and* (**4**)·1.5CHCl$_3$

	(**1**)·2CH$_2$Cl$_2$	(**2**)·2CHCl$_3$	(**3**)·2CHCl$_3$	(**4**)·1.5CHCl$_3$
Complex	[Sn(tpp)(OAc)$_2$]· 2CH$_2$Cl$_2$	[Sn(tpp)(OCOCHCl$_2$)$_2$]· 2CHCl$_3$	[Sn(tpp)(OCOCF$_3$)$_2$]· 2CHCl$_3$	[Sn(tpp)(OCOH)$_2$]· 1.5CHCl$_3$
Formula	C$_{50}$H$_{38}$Cl$_4$N$_4$O$_4$Sn	C$_{50}$H$_{32}$Cl$_{10}$N$_4$O$_4$Sn	C$_{50}$H$_{30}$Cl$_6$F$_6$N$_4$O$_4$Sn	C$_{47.5}$H$_{31.5}$Cl$_{4.5}$N$_4$O$_4$Sn
M	1019.33	1225.99	1196.17	1000.48
Crystal System	monoclinic	triclinic	triclinic	triclinic
Space Group	$P2_1/n$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a, Å	9.1098(1)	9.7110(4)	9.7788(4)	11.5205(3)
b, Å	11.6176(1)	11.0179(2)	11.1308(5)	17.7654(4)
c, Å	20.7143(2)	11.9082(6)	11.6314(5)	22.6359(5)
α, deg.		96.311(3)	95.895(3)	73.5727(18)
β, deg.	98.268(1)	93.681(4)	103.542(4)	86.7216(17)
γ, deg.		100.502(3)	93.874(3)	76.0304(18)
V, Å^3	2169.49(4)	1240.55(9)	1218.82(9)	4311.96(18)
D_c, g·cm^{-3}	1.560	1.641	1.630	1.541
Z	2	1	1	4
Colour	purple	purple	purple	purple
Habit	rectangular prism	rectangular prism	multi-faced block	multi-faced blocks
Dimensions, mm	0.32 × 0.25 × 0.15	0.46 × 0.30 × 0.09	0.40 × 0.35 × 0.30	0.22 × 0.17 × 0.11
μ(MoK_α), mm^{-1}	0.888	1.104	0.926	0.922
$T_{min,max}$	0.812, 0.875	0.676, 0.905	0.693, 0.757	0.675, 0.904
N_{ind} (R_{int})	5085 (0.0187)	5453 (0.0217)	5327 (0.0189)	20187 (0.0506)
$N_{obs} - (I > 2\sigma(I))$	4300	4809	4931	14984
N_{var}	287	313	322	1121
$R1$ [A], $wR2$ [A]	0.027, 0.058	0.028, 0.054	0.0371, 0.0806	0.060, 0.120
A, B	0.01, 3	0.01, 1	0.01, 3	0.004, 20
GOOF	1.011	1.006	1.057	1.096
$\Delta\rho_{min,max}$, e·Å^{-3}	–0.699, 0.648	–0.506, 0.526	–1.141, 1.534	–1.69, 1.85

[A] Reflections with $[I > 2\sigma(I)]$ considered observed. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR2_{(all)} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (\mathbf{A}P)^2 + \mathbf{B}P]$, $P = (F_o^2 + 2F_c^2)/3$.

tails). ORTEP representations of (**2**)·2CHCl$_3$ and (**3**)·2CHCl$_3$ are provided in Fig. 2. As in (**1**)· ·2CH$_2$Cl$_2$, the complexes reside on crystallographic inversion centres.

The diformato complex has a somewhat unusual crystal structure. The space group is $P\overline{1}$, and the asymmetric unit contains two formula units of the complexes made up from two half molecules on $\overline{1}$ special positions and one entire molecule with no crystallographic symmetry. No suitable higher symmetry models were found. The asymmetric unit also contains three chloroform molecules, two of which are disordered: C(94), Cl(4)—Cl(6) modelled in two positions with occupancies 0.8 and 0.2, and C(95), Cl(7)—Cl(9) also modelled in two positions but with occupancies of 0.55 and 0.45. An ORTEP representation showing the crystallographically independent molecules is shown in Fig. 3. Ball and stick style representations of the coordination spheres around each of the independent Sn(IV) atoms demonstrate that the molecules in this structure are in every other respect similar to (**1**), (**2**) and (**3**). The only exception is a slight conformational difference between the orientations of the two formato ligands with respect to each other in the asymmetric molecule associated with Sn(2).
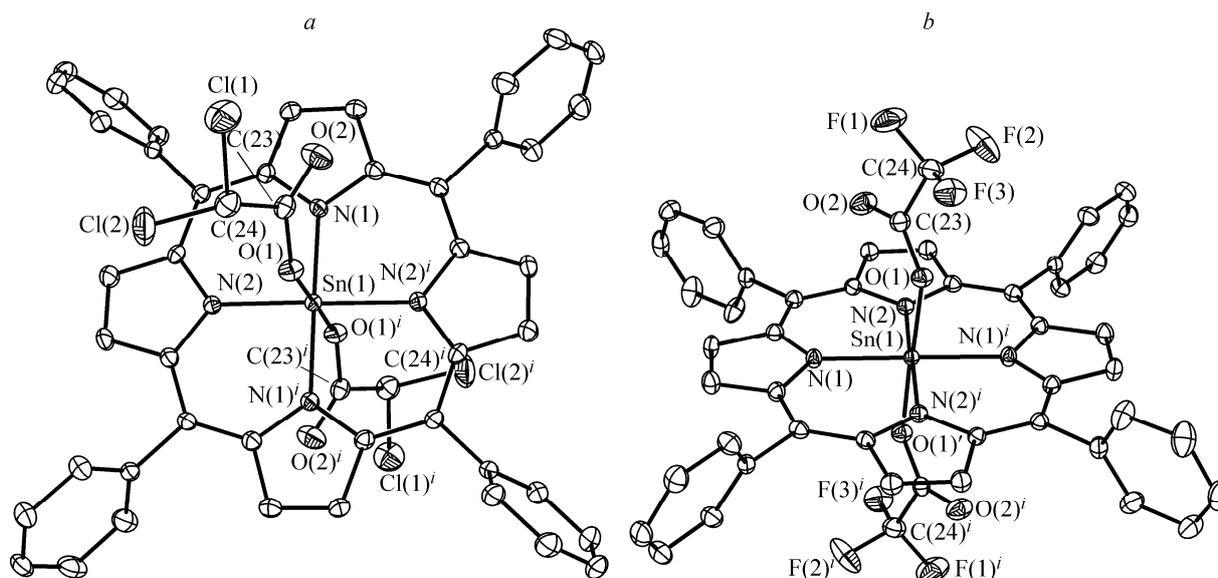
Fig. 2. ORTEP representations of the isostructural compounds (*a*) (**2**)·2CHCl$_3$ and (*b*) (**3**)·2CHCl$_3$. In each case Sn(1) resides on an inversion centre. Hydrogen atoms and chloroform molecules have been omitted for clarity. Thermal ellipsoids are drawn with 40 % displacement probability. Symmetry operation: ^{i} −*x*+1, −*y*+1, −*z*+1
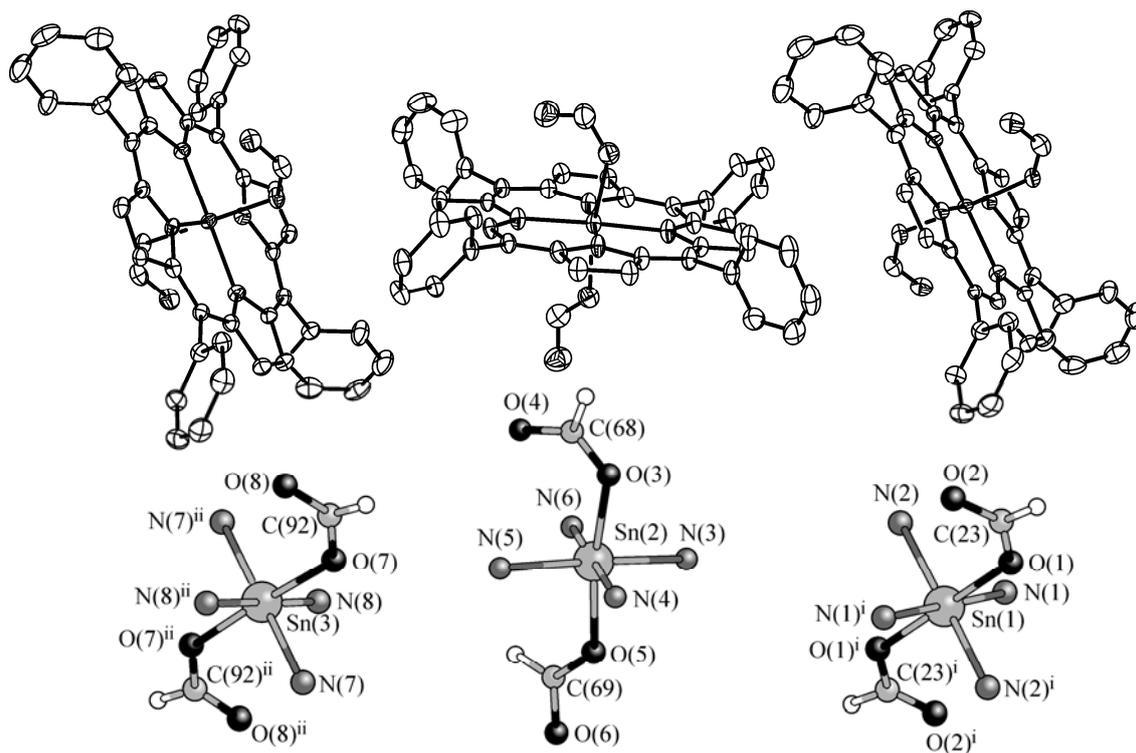

Fig. 3. ORTEP depictions of the three crystallographically independent molecules in (**4**)·1.5CHCl$_3$. The relative spatial arrangement of the molecules is as illustrated. The complexes comprising Sn(1) and Sn(3) have inversion symmetry while the complex comprising Sn(2) is asymmetric. Thermal ellipsoids are drawn with 40 % displacement probability. Hydrogen atoms, chloroform molecules and atom labels have been omitted from the thermal ellipsoid plots for clarity. The atoms of the coordination spheres (including pertinent atom labels) are illustrated below each molecule in approximately the same orientation. Symmetry operations: ^{i} −*x*, −*y*+2, −*z* and ^{ii} −*x*, −*y*, −*z*+1

Sn—N *and* Sn—O *bond lengths for tin*(IV) *porphyrin complexes with anionic* O-*bound axial ligands*

Ligand X$^-$	Porphyrin	d Sn—N (av), Å	d Sn—O (av), Å	Reference
OH	tpp	2.106	2.017	24
OAc	tpp	2.091	2.096	this work
Acsal[a]	tpp	2.10	2.08	24
OBz	tpp	2.087	2.086	24
OCOH	tpp	2.086	2.090	this work
sal[b]	tpp	2.09	2.055	24
OCOCHCl$_2$	tpp	2.084	2.091	this work
OCOCF$_3$	tpp	2.082	2.109	this work
NO$_3$	tpp	2.08	2.113	23
ClO$_4$	tpp	2.073	2.181	30
OCO-1-Nap[c]	tpp	2.106	2.095	31
OCOFc[d]	tpp	2.094	2.073	32
1-ONap[e]	tptp[f]	2.089	2.085	33
2-ONap[g]	tptp	2.097	2.062	34
OPh	tptp	2.09	2.055	10
OPh-4-NO$_2$	tptp	2.09	2.083	35
OPh-2-NO$_2$	tptp	2.09	2.07	10
OPh-2-OH	tptp	2.086	2.097	9
OMe	tpOMepp[h]	2.10	2.01	36
OAc	tpOMepp	2.093	2.103	37
OCOEt	tpClpp[i]	2.084	2.093	38
OCOCHC$_{60}$	t(3,5-di-*t*-Bu)pp[j]	2.090	2.116	39
OH	tpyp[k]	2.101	2.014	40
OH	tpyp	2.108	2.027	3
OCO-4-py	tpyp	2.091	2.087	41

[a] Acetylsalicylato;
[b] salicylato;
[c] 1-naphthylcarboxylato;
[d] ferrocenecarboxylato;
[e] 1-naphthoxo;
[f] 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato;

[g] 2-naphthoxo;
[h] 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrinato;
[i] 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrinato;
[j] 5,10,15,20-tetrakis(3,5-di-*t*-butylphenyl)porphyrinato;
[k] 5,10,15,20-tetrakis(4-pyridyl)porphyrinato.

The data for Sn—O and Sn—N bond lengths for complexes (**1**)—(**4**) are listed in Table 2, together with the data for all examples of complexes of tin(IV) tetraarylporphyrins with O-bound anionic ligands. The majority of examples are for tpp complexes, while data are also available for some 4-methyl-, 4-methoxy-, 3,5-di-*t*-butyl- and 4-chlorophenyl analogues, as well as recently for complexes of tetrakis(4-pyridyl)porphyrin. The previously published values [25] for the complex (**1**) are not included in the table. These collected data cover a wide range of ligand basicity, from perchlorate to methoxide and hydroxide. The rest of the complexes fall into three classes, namely carboxylates, aryloxides and the unique nitrate. Our new data for the dichloroacetate **2** and trifluoroacetate **3** extend the pK_a range of the carboxylates into a region not previously available, with pK_a values of 1.26 and 0.59, respectively.

The empirical relationship between the Sn—N and Sn—O bond lengths is shown in Fig. 4, and the approximately inverse relationship is clearly evident, although there is considerable scatter. Thus
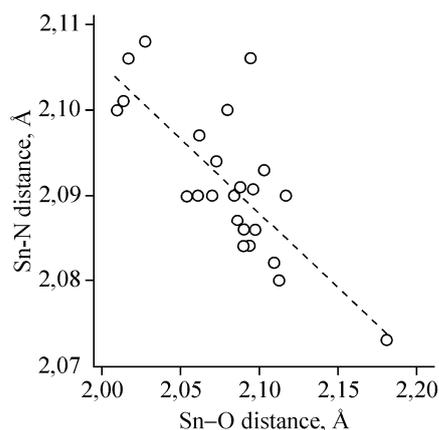
Fig. 4. Comparison of Sn—N and Sn—O bond lengths for all known tin(IV) porphyrin complexes with axial anionic O-bound ligands
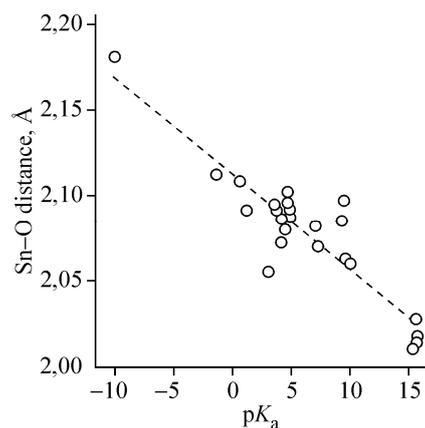
Fig. 5. Correlation of Sn—O bond lengths with the pK_a of the conjugate acids of the axial ligands for Sn(IV) porphyrin complexes with axial anionic O-bound ligands

as the electron demand of the axial O-ligands increases, the Sn—N core generally expands. The porphyrin ring is able to accommodate Sn—N bond lengths covering the range 2.073 Å (X = perchlorato) to 2.108 Å (X = hydroxo) without significant out-of-plane distortion of the ring. For the former, the largest displacement from the mean $C_{20}N_4$ plane is 0.098 Å for a β carbon [30], while for the latter, the largest displacement from the mean $C_{20}N_4$ plane is 0.085 Å also for a β carbon [3]. The ligand whose data point lies farthest from the line of best fit is 1-naphthylcarboxylato, whose Sn—N length is longer than expected [31]. A specific reason for this deviation is not obvious. A better empirical correlation is found for relationship between the Sn—O bond length and the pK_a of the conjugate acid of the axial ligand (Fig. 5). The correlation coefficient is –0.91. Clearly ligands that are more basic have shorter Sn—O bond lengths (and generally longer Sn—N bonds). This relationship is good evidence that the bonding to the highly charged Sn(IV) centre is sensitive mostly to electrostatic effects, and the tin(IV) porphyrin centre is a typical hard acid.

CONCLUSIONS

The crystal structures of four Sn(IV) porphyrin complexes with acetate, dichloroacetate, trifluoroacetate and formate as axial ligands have been determined. The Sn—N and Sn—O bond lengths for these and all other reported similar structures have been compared and the Sn—O bond lengths correlated with the pK_a of the conjugate acids of the axial anionic ligands. The oxophilic Sn(IV) centre behaves as a typical hard acid centre.

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